

Optimization of DPC Process Applied by Electroless Copper Plating

Xinnang Lang

Huazhong University of Science and Technology

Abstract: With the continuous improvement of chip power, the area is shrinking and the integration is getting higher and higher. The LED package puts higher requirements on the heat dissipation substrate. Direct plated copper (DPC) is fabricated on a ceramic substrate by a thin film process. It has stable chemical properties, high thermal conductivity, fine wiring, and a coefficient of thermal expansion (CTE) matching the chip material. The important development direction of power LED package heat sink substrate. However, due to the high price of DPC substrates, there is no corresponding quality and testing standards, which limits its application in high-power LED packaging. In this thesis, electroless copper plating on ceramic surface is used as the seed layer of DPC substrate, which reduces the costly equipment and process such as magnetron sputtering, and reduces the manufacturing cost of DPC substrate. Pulse plating instead of DC plating thickens the copper layer line, which not only improves the efficiency. At the same time, the quality of the coating is optimized; the silver layer is replaced by the gold layer as the soldering layer and the protective layer to reduce the material cost; and compared with other types of ceramic substrates, some test methods for the performance of the DPC substrate are proposed to further standardize the DPC substrate quality standard. Explored. The relationship between the current density of pulse copper plating and the plating rate was analyzed. The results show that the two are proportional to each other within a certain range. At the same current density, pulse plating can significantly reduce the formation of the tumor-like structure and optimize the quality of the coating compared to DC plating. The current density of 3ASD not only improves the plating efficiency, but also obtains a well-formed circuit layer.

Keywords: DPC; electroless copper plating; pulse copper plating

1. DPC process using electroless copper plating

Sputter deposition of the seed layer requires expensive equipment and vacuum environment, and the cost is high, and the electroless copper plating technique is used to deposit the seed layer, which is simple in operation, high in efficiency, and low in cost^[1]. The electroless copper plating layer is the DPC process flow of the seed layer. The ceramic substrate used in this experiment is alumina ceramic, and the laser drilling process is not performed.

Firstly, the ceramic substrate is prepared and the cleaning process is completed; then the deposition of the seed layer is performed by an electroless copper plating process, the thickness is about 500 nm; the dry film type is DuPont SD250, and the dry film is attached to the ceramic piece to minimize the generation of bubbles. Curing at 60 °C for 10 min on a hot plate; completing the exposure process on a lithography machine, then placing the ceramic piece in a developing solution, developing a solution of 3% Na₂CO₃ to obtain a desired line pattern; using copper methane sulfonate Plating liquid plating thickening copper layer line; plating a layer of metallic nickel to protect the copper layer from oxidation, and also preventing active copper ions from entering the gold layer through the interface, affecting the weldability of the gold layer; depositing by sputtering process The gold layer improves the soldering performance of the

Copyright © 2018 Xinnang Lang.

doi: 10.18063/jcra.v1i1.

This is an open-access article distributed under the terms of the Creative Commons Attribution Unported License

(<http://creativecommons.org/licenses/by-nc/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

ceramic substrate; finally, the excess dry film is removed by using the degumming solution (3-5% Na OH solution); finally, the seed layer is removed by using a mixture of hydrogen peroxide and hydrochloric acid. The entire process is completed, the DPC ceramic substrate is cleaned, the substrate is dried by nitrogen, diced, and sealed. 2 pulse copper plating

2. Line thickening problem in DPC process

In the DPC process using electroless copper plating, in order to ensure the electrical properties of the circuit layer, the thickness of the copper layer is usually required to be about 30 μm , and in practical applications, it can reach more than 50 μm . Since the thickness of the seed layer is about 500 nm, the thickening line is a DPC process. An important step in the process. Electroplating is a process of depositing a layer of metal or alloy on the cathode material by electrolysis. The electroplating efficiency is high, and the obtained coating layer is dense, which is the main means for thickening the circuit layer in the current DPC process. In this experiment, the copper plating solution was made of copper methanesulfonate plating solution and the current density was 1.5 ASD (A/dm^2). The line thickening process was completed. It was found that during the electroplating process, many tumor-like structures appeared on the surface of the coating, especially in the plating process. There are more granular structures on the edges, as shown in **Figure 1-1**:

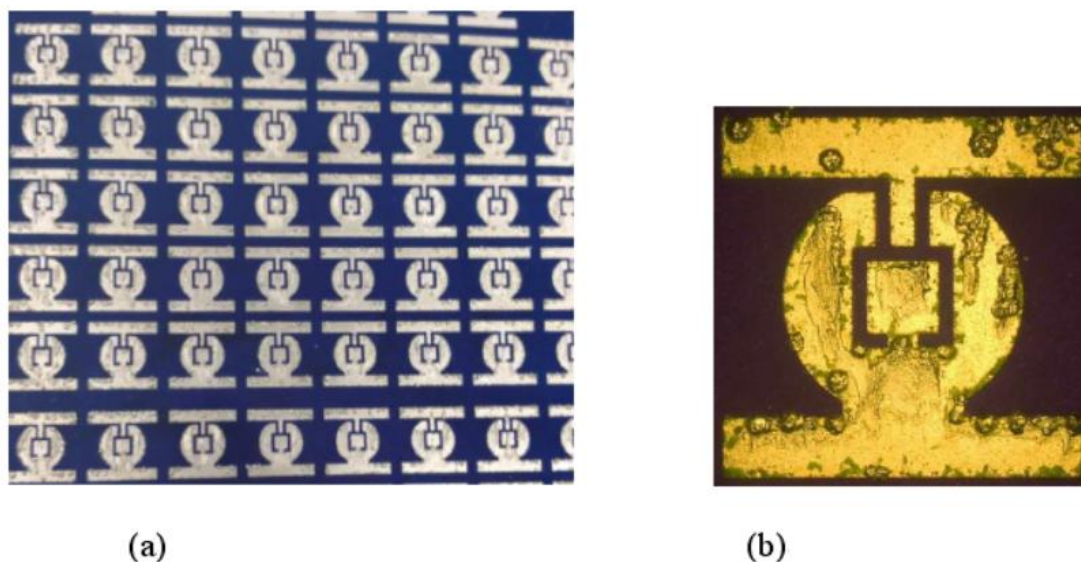


Figure 1-1 Tumor structure of the plated surface

The surface quality of the electroplated copper layer is directly related to the current density and plating time. In order to analyze the causes of the coating structure, these two key factors are used to design the two schemes. First, the plating time is constant, and the current density is gradually reduced from 1.5 ASD to 0.5 ASD. The results show that the tumor-like structure gradually decreases and disappears, but the copper layer gloss decreases and the efficiency is low. Second, determine At the time when the tumor-like structure appeared, the current density was kept at 1.5 ASD, and the sample was taken every ten minutes, and the observation was observed, and it was found that the tumor-like structure was produced very little. The first experimental results show that proper reduction of current density can optimize the surface topography, but it will reduce the plating efficiency. In the second experiment, the plating time has not changed, and the current density has not changed, but the current is interrupted every ten minutes for a period of time. The appearance is improved. The reason should be that the edge of the pattern is easy to accumulate more electrons during the electroplating process, the grain growth rate is too fast, and the tumor shape is formed. When the current is interrupted for a while, the edge effect will decrease, so the surface morphology is improved. Considering these two factors, the seed layer in the DPC process is pre-plated with 0.5 ASD for 10 min, then the current is increased to 1.5 ASD, and it is disconnected every ten minutes to achieve a good morphology. However, this process is troublesome. The

efficiency is not high, considering that the circuit on-off is equivalent to a pulse effect, so consider using pulse plating instead of DC plating to optimize the coating morphology.

2.1 Pulse plating introduction

During DC plating, the plating solution on the surface of the cathode is continuously consumed, and the new plating solution cannot be quickly replenished, so that a very poor concentration is formed at the cathode, thereby limiting the deposition speed of the plating layer and increasing the current density, thereby not effectively improving the plating rate. It also causes the surface of the coating to deteriorate, and defects such as pitting and bubbles appear. Pulse plating^[2] uses the on-off of current to reduce the concentration difference, improve the activation polarization of the cathode, thereby improving the plating efficiency and improving the quality of the coating.

Compared with DC electroplating, the advantages of pulse electroplating are mainly reflected in four aspects: dense coating, uniform grain, high conductivity^[3]; improve plating efficiency by reducing the difference in cathode concentration; improve coating quality; improve coating purity. At the same time, the use of additives can be appropriately reduced. The waveforms of pulse plating mainly include square waves, triangular waves^[4], etc., in which square waves are easy to control, and the actual plating effect is good, so it is widely used. The main parameters of the square wave are: on-time t_{on} , off-time t_{off} , pulse period T (pulse frequency f), duty ratio $\gamma = t_{on}/(t_{on}+t_{off})$, pulse current density J_p , average current density J_m , **Figure 2-2** shows the schematic diagramL:

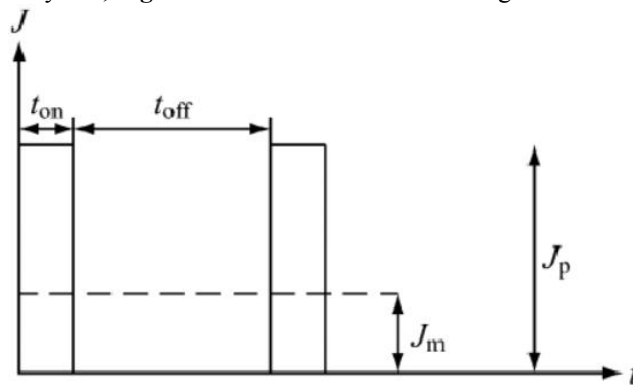


Figure 2-2 Typical square wave diagram

2.2 Pulse plating experiment

In the experiment, copper sulfonate plating solution was used. The power supply was CS electrochemical workstation. The sample was made of pure copper. The plating area was 10mm×30mm. The pulse copper plating parameters were: on-time 80ms, off-time 20ms, duty cycle. The relationship between plating rate and current density was investigated by γ of 80% and period of 100ms (frequency of 10Hz), and the surface morphology of the coating obtained by DC plating and pulse plating at the same current density was compared. **Figure 2-3** shows the experiment. The instrument used.



Figure 2-3 Electrochemical workstation

The current density was 2ASD, 3ASD, 4ASD, 5ASD, 6ASD, and the plating rate and surface quality were investigated by using pure copper sheets with the same material and plating area. The plating rate was calculated in two ways. One method is mass method. That is, the plating speed calculation formula is:

$$r = \frac{\Delta w \times 10^4}{\rho \times S \times t} \quad (1)$$

Where: r-copper plating rate ($\mu\text{m/h}$); w - poor quality before and after plating (g); ρ -copper density (8.93g/cm^3); S-copper area (cm^2); t-plating Time (h).

Another method is the theoretical estimation method of electroplated coating thickness (2), which is the formula 2 in the figure. The results calculated by the two methods are shown in **Figure 2-4.:**

$$T = K \frac{Q \times E}{A \times \rho} \quad (2)$$

Where: T-copper layer thickness (cm); Q-consumption power, $Q=I \times t$, I is average pulse current (A), t-plating time (h); E-electrochemical equivalent ($E_{\text{Cu}}=1.186 \text{ g/A} \times \text{h}$); ρ -copper density (8.93 g/cm^3); A-copper area (cm^2); K-current efficiency, assumed to be 100%.

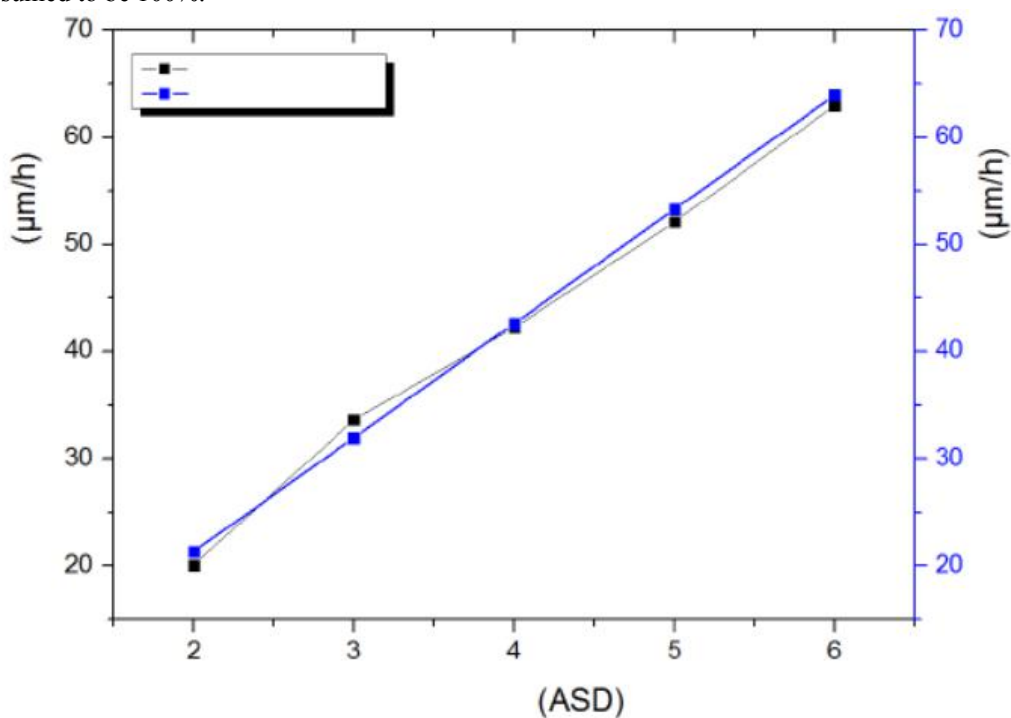


Figure 2-4 Diagram of plating rate and current density

Figure 2-4 shows that the plating rates obtained by the two calculation methods are very close, which indicates that the current efficiency K in the plating thickness estimation formula can be assumed to be 100% when the current density does not exceed 6 ASD, and the plating rate and current density are direct ratio. **Figure 2-5** shows the comparison of the surface topography of DC plating and pulse plating with a current density of 3ASD and an effective plating time of 30 min. (a) The figure shows the shape of the pulse plating, which can be seen at the sharp corners of the coating. A few granular structures, the other edges are well-formed, (b) the figure shows the DC plating topography, and a large number of granular structures appear on the surface edges and sharp corners of the coating, which has seriously affected the coating morphology. In this experiment, the surface topography similar to that of **Figure 2-5(b)** appeared when the pulse current density increased to 5ASD, which indicates that pulse plating can improve the quality of the coating.

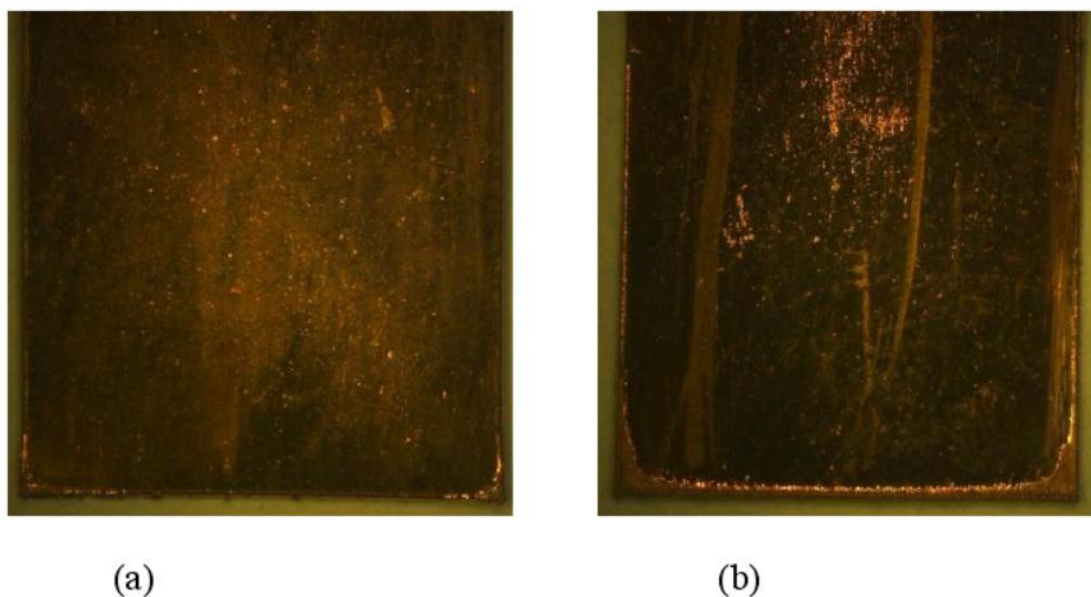


Figure 2-5 Comparison of pulse plating and DC plating

In addition to determining the appropriate pulse current density, this experiment also developed a set of fixtures. As shown in **Figure 2-6**, the clamp current can enter the surface simultaneously from all sides, reducing the average current transmission distance and increasing the surface current distribution of the cathode material. Uniformity is beneficial to obtain a coating with a more uniform thickness and better surface quality.

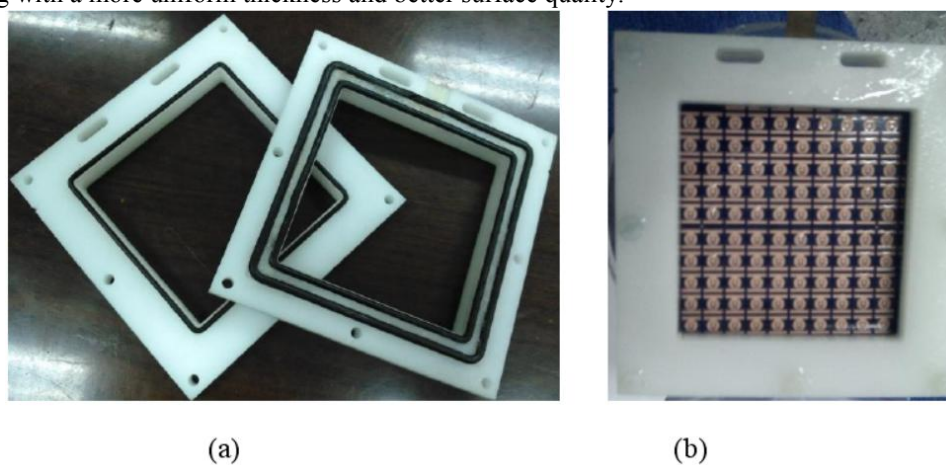


Figure 2-6 Pulse plating sample fixture diagram

Figure 2-7 shows the surface morphology of a DPC substrate with a clamp current density of 3ASD. The copper layer obtained by pulse plating has high activity and is easily oxidized. Therefore, a layer of nickel is required as a protective layer. It is thinner, so the morphology after nickel plating is basically the same as that of the copper plating

layer. It can be seen from the figure that the surface of the coating has completely disappeared, and the surface of the coating is flat and the effect is good. The efficiency is obviously improved compared with the current density of 1.5 ASD.

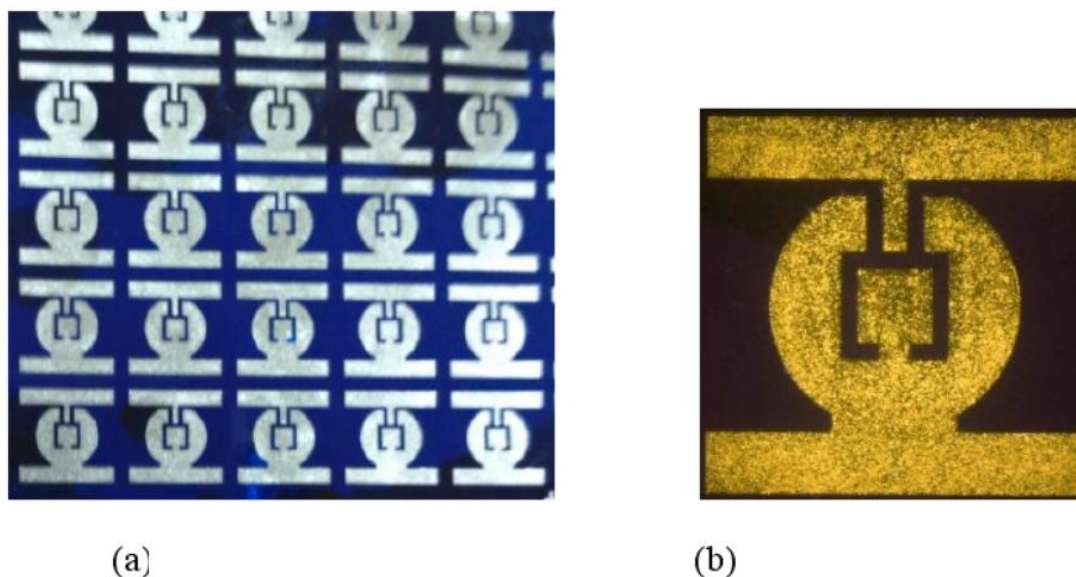


Figure 2-7 Pulse plating surface topography

3. surface silver plating technology

3.1 Electroplating silver process

In the DPC ceramic substrate manufacturing process, a gold layer is usually sputtered on the surface of the substrate, which can improve the soldering performance of the substrate, and on the other hand, the gold layer is stable and protects the substrate from the external environment. Gold as a precious metal, the price is higher, and silver is also a precious metal, the price is relatively low, and the silver layer has good light reflectivity, strong electrical and thermal conductivity, and excellent welding performance. Therefore, it is considered to replace the surface of the DPC ceramic substrate with a silver plating layer^[5]. The sputtered gold layer acts as a protective layer and a solder layer, reducing material costs.

The cyanide silver plating technology was born in 1938. The cyanide silver plating layer has fine grain and excellent performance, but the cyanide is highly toxic. In order to improve the silver plating process, the cyanide-free silver plating technology is constantly being researched and developed^[6]. In this experiment, silver thiosulfate is used for plating. The plating solution is simple in formula, high in use efficiency, and the solderability of the silver layer is good. The process formula and use conditions are shown in Table 3-1. The plating solution must be arranged according to the operation sequence: First, ammonium thiosulfate, silver nitrate and anhydrous sodium sulfite are dissolved in a certain amount of deionized water; secondly, an anhydrous sodium sulfite solution is added to the silver nitrate solution to form a silver sulfite turbid liquid accompanied by a yellow precipitate. Then, the turbid liquid is slowly poured into the ammonium thiosulfate solution to form a yellowish solution; finally, after the configured plating solution is allowed to stand overnight, ammonium acetate and thiosemicarbazide are added to replenish the plating solution to a prescribed volume. In its formulation, silver nitrate acts to provide Ag^+ ; ammonium thiosulfate and anhydrous sodium sulfite are used as complexing agents to prevent the anion from being naturally oxidized, resulting in failure of the plating solution; ammonium acetate acts to adjust the pH value; thioamino Urea action promotes anodic dissolution and refines grains^[7].

The power source used in the experiment is the CS electrochemical workstation of the Kesite instrument. The constant current source is used. The sample is cleaned copper and nickel-plated copper. The water bath provides a constant temperature of 25 °C, current density and plating time respectively. The 0.25ASD, 15min, plating solution and other process conditions are consistent with Table 3-1, the experimental results are shown in **Figure 3-1**.

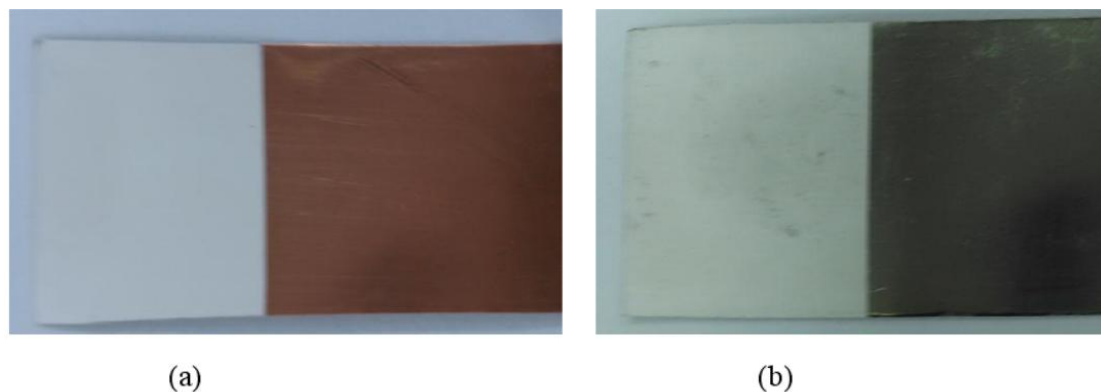


Figure 3-1 Appearance of silver plating

During the experimental operation, the sample should be charged into the plating solution. Because the potentials of copper and nickel are higher than silver, the silver can be directly replaced, and the displaced silver has poor adhesion to the substrate. **Figure 3-1(a)** shows the silver plating on the surface of the pure copper layer, and (b) shows the silver plating process on the nickel layer. The results show that the thiosulfate silver plating solution can be realized on the copper substrate and the nickel substrate. The silver layer obtained on the copper substrate is more bright, and the surface morphology of the silver layer is observed under an optical microscope. It can be seen that the surface structure of the silver layer is uniform, no obvious defects exist, and the effect is good.

3.2 Electroplating silver layer composition analysis

Samples were analyzed using X-ray fluorescence probes (XRF) and energy dispersive spectroscopy (EDS). **Figure 3-2** shows the XRF test results. Due to the strong X-ray penetration, the three components of the sample are copper, nickel, and silver. All tested, in order to further determine that the silver layer does not contain copper and nickel, continue to analyze the composition using EDS

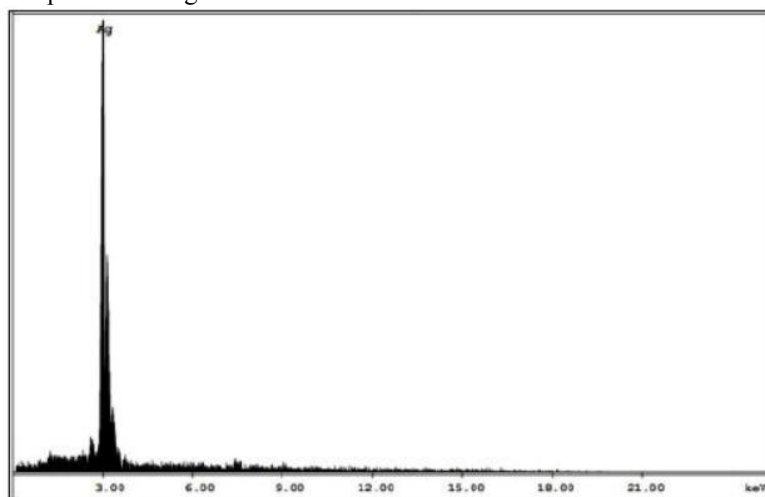


Figure 3-3 Silver-plated sample EDS test

3.3 Silver layer binding analysis

The good bonding force between the silver layer and the substrate is the basic guarantee for the performance of the silver layer. The 3M method is the most commonly used method for film bonding test. For the bonding of ink layers such as printing and silk screen printing, it is necessary to use a hundred-grain knife. After the test, the metal film can be directly adhered to observe whether there is obvious peeling off. The result is shown in **Figure 3-4**: (a) The figure shows the peeling of the silver plating on the copper layer. After the 3M tape is pulled up, The large peeling of the silver layer indicates that the bonding strength between the silver layer and the copper layer is relatively poor; (b) the peeling

area of the silver plating layer on the nickel layer is significantly smaller than (a), indicating that the bonding strength between the nickel layer and the silver layer is good, but still There are many places falling off, considering whether it is the cause of excessive current density. Therefore, a new silver layer is obtained by applying a current density of 0.2 ASD on the nickel layer for 30 min. The test results are as shown in (c), the silver layer. The shedding area is very small and passed the 3M test. The analysis of the bonding strength of the silver layer shows that the bonding force between the nickel layer and the silver layer is better than that of the copper layer and the silver layer. Therefore, plating a layer of nickel before the silver plating layer helps to improve the bonding force, and It was finally determined that the current density used for electroplating was 0.2 ASD.

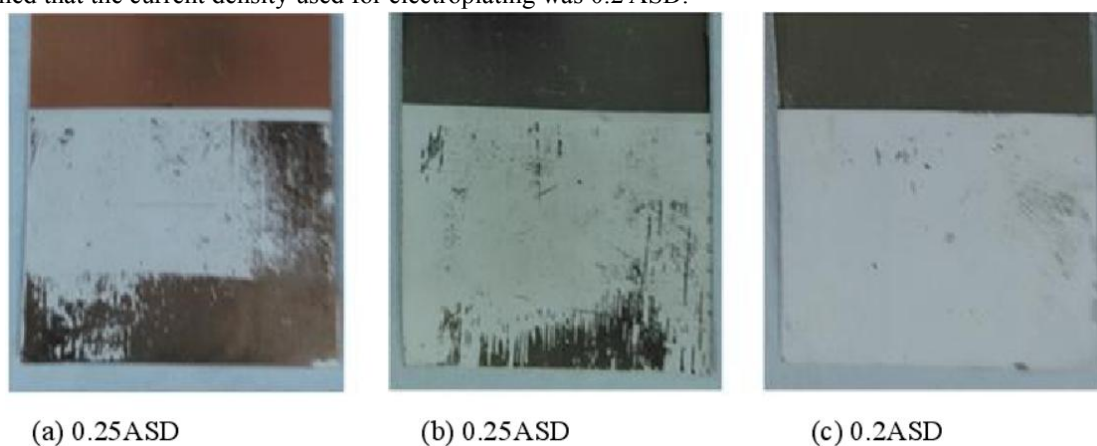


Figure 3-4 Silver adhesion test results

3.4 Gold wire bonding

DPC ceramic substrate and chip are electrically interconnected by gold wire, so the silver layer on the surface of the substrate should have good soldering performance, and the metal silver itself has excellent soldering performance, and the wire bonding machine is used for gold wire bonding on the surface of the silver layer. The effect is shown in **Figure 3-5**. The gold wire can be welded well with the silver layer, and it can be seen from the figure that the surface of the silver layer is smooth and has no obvious defects.



Figure 3-5 Wire bonding effect diagram

3.5 High temperature test

In the DPC process, the copper line is prevented from oxidizing by applying a nickel plating layer, and the analysis of the bonding force determines that the nickel layer not only protects the copper layer but also improves the bonding force with the silver layer. The sample was placed on a hot plate and baked at 300 ° C for 10 min. It was found that the silver layer on the copper layer turned yellow, while the silver layer on the nickel layer did not change significantly, indicating that the silver layer turned yellow because of the active copper element. Entering into the silver layer affects

its resistance to discoloration, and the nickel layer can well block the diffusion of copper ions into the silver layer, so the nickel-plated sample has strong high temperature resistance.

4. Conclusion

In this paper, the morphology of the pulsed copper layer and the DC electroplated copper layer are compared at the same current density. The results show that pulse plating can effectively reduce the tumor-like structure on the surface of the coating. Secondly, the relationship between current density and plating rate is investigated. In the case of no more than 6ASD, the two are proportional to each other. Pulse plating not only improves the plating efficiency, but also improves the quality of the coating. Finally, silver is electroplated on the copper layer and the nickel layer respectively. The performance analysis shows that the copper layer is first plated. A layer of nickel is used to electroplate the silver layer with a current density of 0.2 ASD to obtain a silver layer with good adhesion and good discoloration resistance.

References

- 1 Mu D., Jin Y. .Study of anodized Al substrate for electronic packaging. Journal of Materials Science: Materials in Electronics, 2000, 11(3): 239-242.
- 2 Chene O. , Landolt D. . The influence of mass transport on the deposit morphology and the current efficiency in pulse plating of copper. Journal of applied electrochemistry, 1989, 19(2): 188-194.
- 3 Emekli U. , West A. C. . Effect of additives and pulse plating on copper nucleation onto Ru. Electrochimica acta, 2009, 54(4): 1177-1183.
- 4 Yung K. C. , Yue T. M. , Chan K. C. , *et al.* The effects of pulse plating parameters on copper plating distribution of microvia in PCB manufacture. Electronics Packaging Manufacturing, IEEE Transactions on, 2003, 26(2): 106-109.
- 5 Rivera I., Roca A. , Cruells M. , *et al.* Study of silver precipitation in thiosulfate solutions using sodium dithionite. Application to an industrial effluent. Hydrometallurgy, 2007, 89(1): 89-98.
- 6 Zarkadas G. M. , Stergiou A. , Papanastasiou G. . Influence of citric acid on the silver electrodeposition from aqueous Ag NO₃ solutions. Electrochimica acta, 2005, 50(25): 5022-5031.
- 7 Yang C. T. , Liu W. C. , Liu C. Y. . Measurement of thermal resistance of first-level Cu substrate used in high-power multi-chips LED package. Microelectronics Reliability, 2012, 52(5): 855-860.